

CERTIFICATION REPORT

Certification of the mass concentrations of ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate, and of pH and conductivity in simulated rainwater

Certified Reference Material ERM[®]-CA408

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Certified Reference Material ERM[®]-CA408

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Summary

This report presents the preparation and certification of the simulated rainwater certified reference material ERM-CA408. All the steps required for the production of this water-matrix certified reference material are described in detail, from the preparation of the simulated rainwater until the characterization exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2]. Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison among several experienced laboratories. IRMM organised and coordinated all the phases of this project including evaluation of data. The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, see below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and stability.

SIMULATED RAINWATER		
	Mass Concentration	
	Certified value ²⁾ [mg/L]	Uncertainty ³⁾ [mg/L]
Ammonium	0.910	0.028
Chloride ¹⁾	1.96	0.07
Fluoride	0.194	0.008
Magnesium	0.145	0.022
Nitrate	2.01	0.09
<i>Ortho</i> -phosphate	1.00	0.05
Sulfate ¹⁾	1.46	0.04
	Electrochemical property	
	Certified value ²⁾ [μS/cm]	Uncertainty ³⁾ [μS/cm]
Conductivity (20 °C)	18.7	1.8
	Chemical property	
	Certified value ²⁾	Uncertainty ³⁾
pH (20 °C)	6.3	0.6
1) as obtained by ion chromatography coupled with conductimetric detection 2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values and their uncertainties are traceable to the International System of Units (SI). 3) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) with a coverage factor $k = 2$, corresponding to a level of confidence of about 95 %.		

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Glossary

ANOVA	analysis of variance
α	significance level
BCR	Community Bureau of Reference
CFA	continuous flow analysis
CRM	certified reference material
DT	double Grubbs test
Δ_m	absolute difference between mean measured value and certified value
ERM	European Reference Material
IC-CD	ion chromatography with conductimetric detection
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
ISE	Ion Selective Electrode
k	coverage factor
MS_{between}	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per bottle
PTFE	polytetrafluoroethylene
QC	quality control
RSD	relative standard deviation
RSE	relative standard error ($=RSD/\sqrt{n}$)
s	standard deviation
s_{bb}	between-bottle standard deviation
SFA	segmented flow analysis
SI	International System of Units
PHOT	spectrophotometry
ST	single Grubbs test
s_{wb}	within-bottle standard deviation
$t_{\alpha,df}$	critical t -value for a t -test, with a level of confidence equal to $1-\alpha$ and df degrees of freedom
t_{sl}	shelf life
u_{bb}	standard uncertainty related to possible between-bottle heterogeneity
u_{bb}^*	standard uncertainty of heterogeneity that can be hidden by method repeatability
u_{Δ}	combined standard uncertainty of measurement result and certified value
u_{char}	standard uncertainty related to characterization
u_{CRM}	combined standard uncertainty of a certified value
U_{CRM}	expanded uncertainty of a certified value
u_{Its}	standard uncertainty related to long-term stability
u_m	standard uncertainty of a measurement result
u_{rect}	standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
x_i	time point of a stability study
\bar{x}	average of all time points of a stability study
\bar{y}	average of all results of the homogeneity study

1. Introduction

The monitoring of rainwater is fundamental for at least two aspects: on one hand, groundwater reservoirs are replenished by rainfall; on the other hand, wet deposition gives insights in air pollution.

Groundwater is a crucial source of drinking water, supplying the water systems for about two-thirds of European Union citizens.

The legislative framework for its effective protection is established by the Water Framework Directive (WFD, 2000/60/EC) [4] which addresses inland surface waters, transitional waters, coastal waters and groundwater.

A Groundwater "daughter" Directive (2006/118/EC) [5] was adopted (12th December 2006) by the European Parliament and Council on the protection of groundwater against pollution and deterioration, strengthening the existing Groundwater Directive (80/68/EEC) [6] to be repealed in 2013.

This new directive establishes a regime which sets underground water quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater, including criteria for the identification and reversal of significant and sustained upward trends in pollutant concentrations.

On the other hand, the WFD recognises the importance of the cycle linking groundwater and surface waters and it specifies that good status - in both quantity and chemical terms - of a groundwater body also means protecting the surface water bodies and terrestrial ecosystems that depend on its waters.

In the framework of the Convention on Long-Range Transboundary Air Pollution (CLRTAP), there is an international control instrument called European Monitoring and Evaluation Program (EMEP), a scientifically based and policy driven monitoring program aiming to investigate and solve long-range transboundary air pollution [7]. In this program, more than one hundred stations in 25 countries operate a wet-only deposition measurement network to monitor inputs of air pollutants transported over long distances and across national borders reaching soil, vegetation and surface water via precipitation. Weekly rainwater samples are collected: chemical and physical analysis covers the parameters sulfate, nitrate, ammonium, chloride, sodium, potassium, magnesium and calcium as well as pH value and conductivity.

These measurements serve to monitor pollution over large areas and to verify the effectiveness of pollution abatement measures.

The Chemical Co-ordinating Centre (CCC) of EMEP hosted by the Norwegian Institute for Air Research (NILU) has within its tasks the maintaining and improvement of quality assurance programmes to make sure that observation data are of known quality and adequate for their intended use.

The confidence in any assessment on pollution, related either to groundwater or to air, will depend on the quality in the context of measurement data. A continuous quality assurance system should therefore be developed and implemented for each monitoring institution to ensure that the reported results meet assured target levels of precision and bias [8].

The availability of appropriate certified reference materials will be an asset in the validation of analytical methods, ensuring accuracy and traceability of the measurement results.

The European Commission's Community Bureau of Reference (BCR) issued two simulated rainwater CRMs (CRM-408 and 409) in 1993. The production of ERM-CA408 was carried out by IRMM and is described in the present report, is intended to be the replacement for these two materials and to be used as quality assurance and quality control tool by the monitoring laboratories.

General information

The parameters certified in ERM-CA408 are commonly referred to as major components or major elements of the water and are the following: ammonium, calcium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate. The properties conductivity and pH are also certified. The certified values are stated as mass concentrations, milligrams per liter (mg/L) because this is the most common way used by the "water analysis" community to express concentration of a substance in water. Conductivity value is expressed in $\mu\text{S}/\text{cm}$ while for pH value no unit is applicable.

2. Participants

- Sampling and processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, BELAC-268-TEST)

- Homogeneity study

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

- Stability studies

DVGW-Technologiezentrum Wasser, Karlsruhe, DE

(accredited to ISO/IEC 17025 for measurements of chemical parameters in groundwater, DACH DAC-PL-0142 -01-10)

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE

(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

- Characterisation analyses

ALS Czech Republic s.r.o., Praha, CZ

(accredited to ISO/IEC 17025 for chemical analysis of water, CAI No 521/2008)

Bayer Antwerpen NV, Centraal Laboratorium, Antwerpen, BE

(accredited to ISO/IEC 17025 for chemical analysis of water, BELAC No 264-TEST)

Chemservice SRL, Novate Milanese, IT

(accredited to ISO/IEC 17025 for chemical analysis of groundwater, SINAL No 0004)

Consiglio Nazionale delle Ricerche, Istituto per lo Studio degli Ecosistemi, Verbania Pallanza, IT

DVGW-Technologiezentrum Wasser, Karlsruhe, DE

(accredited to ISO/IEC 17025 for measurements of chemical parameters in groundwater, DACH DAC-PL-0142 -01-10)

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE

(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

Laboratoire National de métrologie et d'essais, LNE, Paris, FR

(accredited to ISO/IEC 17025 for measurement of pH in reference standard solutions, Cofrac, No 2-54)

Macaulay Land Use Research Institute, Aberdeen, UK

(accredited to ISO/IEC 17025 for analysis of chemical parameters in natural waters, UKAS No 1917)

Rijkswaterstaat, Ministerie van Verkeer and Waterstaat, Waterdienst, Lelystad, NL

(accredited to ISO/IEC 17025 for chemical analysis of surface and wastewater, RvA, No L194)

VA SYD, Malmö, SE

(accredited to ISO/IEC 17025 for chemical analysis of freshwater, SWEDAC No 07-213-51.1056)

Vlaamse Instelling voor Technologisch Onderzoek - VITO, Mol, BE

(accredited to ISO/IEC 17025 for chemical analysis of groundwater, BELAC No 045-TEST)

- Project management and data evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, BELAC-268-TEST)

3. Time schedule

Preparation and processing	December 2007
Homogeneity and short-term stability measurements	July 2008
Long-term stability measurements	February 2010
Characterisation measurements	February 2009

4. Processing

4.1 Preparation of the material

Before preparation of the final batch of simulated rainwater, a test on a 5 L sample was conducted to check if the target levels were reached. Analyses for the mass concentration of calcium, potassium, magnesium and sodium were carried out in-house by ICP-OES while analyses for the mass concentration of ammonium, chloride, sulfate, nitrate, *ortho*-phosphate and fluoride, and the measurement of pH and conductivity were carried out by an external laboratory (see Table 1).

Table 1. Preliminary analyses of the simulated rainwater

Parameter	Found concentration [mg/L]	Target concentration [mg/L]
Ammonium	1.0	1.0
Calcium	0.38	0.30
Chloride	2.8	2.0
Fluoride	0.2	0.2
Magnesium	0.19	0.16
Nitrate	2.0	2.0
<i>Ortho</i> -phosphate	0.98	1.04
Potassium	0.16	0.15
Sodium	0.98	1.07
Sulfate	1.5	1.5
pH	4.8 (22 °C)	4 - 5
Conductivity [μ S/cm]	24.8 (25 °C)	~20

The final 200 L batch of reference material was prepared from ultra-pure water (18.2 $\mu\text{S}/\text{cm}$) to which freshly prepared solutions of ammonium chloride 99.995 %, calcium nitrate tetrahydrate 99.95 %, magnesium nitrate hexahydrate, dipotassium hydrogen phosphate anhydrous 99.99 % (all Suprapur, Merck, Darmstadt, DE), sodium nitrate 99.995 % (Sigma-Aldrich Chemie, Steinheim, DE), sodium fluoride 99.99 % (Suprapur, Merck, Darmstadt, DE), sodium sulfate 99.99 %, ammonium dihydrogen phosphate 99.999 % (Sigma-Aldrich Chemie, Steinheim, DE) and diluted HCl (Suprapur, Merck, Darmstadt, DE) were added. The salt solutions were previously filtered using AcroPack™ 1000, Supor® Membrane 0.8/0.2 μm , Pall Corp, Port Washington, NY, US, offering also bacterial retention.

The 200 L drum intended for containing the bulk water before ampouling was very carefully cleaned by rinsing using several media in sequence and then placing the drum in a three-dimensional mixer for thorough mixing (Dyna-MIX CM 200, WAB, Basel, CH). The drum was rinsed with water with a small amount of Triton-X 100®, cyclohexane (twice), denaturated ethanol (twice), diluted HNO_3 ~6 % v/v (twice) and finally extensively flushed with ultra-pure water (3 times in the Dyna-MIX CM-200).

To 100 L ultra-pure water, initially collected in one 200 L polyethylene pre-cleaned drum the filtered salt and acidic solutions were added. Portions of ultra-pure water were subsequently filled into the container to reach the final volume of 200 L (checked by weighing the drum). The pH of the final batch was measured and found to be around 5.0. Homogenisation was achieved by continuous stirring with a PTFE stirrer for several hours. The paddle was pre-cleaned with ~2 % v/v HNO_3 and subsequently rinsed with de-ionised water.

The borosilicate hand-made ampoules of 100 mL were rinsed one by one with de-ionised water and dried at 60 °C in a drying cabinet (Elbanton, Kerckdriel, NL). After drying, and before being used, they were sealed with Parafilm to avoid deposition of dust.

4.2 Ampouling and sterilisation

The PTFE tubes used for transferring the water to the automatic ampouling machine (Rota R910/PA, Wehr/Baden DE) were previously rinsed with ~2 % v/v HNO_3 and subsequently extensively rinsed with de-ionised water. The tubes were also "conditioned" with the simulated rainwater for few minutes, just before starting the ampouling step.

About 97 mL of water was subsequently filled into 100 mL borosilicate glass ampoules. The head-space was flushed with argon before flame-sealing, using an automatic ampouling machine.

Before thermal sterilisation of the CRM-batch several tests had been performed by autoclavation of sealed ampoules. This was done to evaluate the feasibility of this conservation method with respect to sterilisation efficiency and risk of glass breakage. To ensure that the sterilisation process had effectively taken place, 3 ampoules in a batch of 90 were spiked with *Escherichia Coli* (200 CFU/ μ L). To double-check, a biological indicator (3M Attest Biological Indicator 1262/1262P using *Bacillus stearothermophilus* ATCC 7953) was also taped on one of the ampoules. After autoclavation, the spiked water and the indicator were incubated (together with positive and negative controls). The autoclaved and spiked waters were found sterile, thereby confirming the efficiency of the sterilisation process.

On the basis of these tests, the water in the closed ampoules of candidate certified reference material ERM-CA408 was sterilised by autoclavation at 121 °C for 15 minutes (Webeco, Ober-Ramstadt, DE). In total 2 % of the ampoules broke during the sterilisation process. Subsequently, labelling of 1370 units took place. After this step, the ampoules were stored at 18 °C in the dark.

5. Homogeneity study

With the aim of checking the homogeneity of the material with regard to the parameters to be certified, 20 units were chosen using a random stratified sample picking scheme. The number of units is based on the produced batch size (approximately corresponding to the cubic root of the total number of units). The batch is divided into the same number of groups and one unit is picked from each group. These samples were analysed in duplicate for content of ammonium, calcium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, potassium, sodium, sulfate (10 ampoules) and for pH and conductivity at 20 °C (10 ampoules).

The measurements were performed under repeatability conditions, i.e. during one analytical run, using validated methods and according to an imposed random sequence to permit distinction between possible trends in the analytical sequence and in the filling order. Quality control (QC) samples and blank samples were analysed at the beginning, at the end and at various points within the sequence.

Ammonium and *ortho*-phosphate were measured by photometry, calcium, magnesium, potassium and sodium by inductively coupled plasma optical emission spectrometry (ICP-OES), chloride, fluoride, nitrate and sulfate by ion chromatography with conductimetric detection (IC-CD), pH by potentiometry and conductivity by conductimetry, both reported at

20 °C. Sample intakes ranged from 0.1 mL to 25 mL, depending on the analyte and on the technique.

The 20 results of each analyte were evaluated by one-way analysis of variance (ANOVA). The unimodal distribution of data is an important prerequisite in order to apply the ANOVA statistical evaluation, therefore the distributions of sample averages as well as individual results were checked both for normality employing normal probability plots and for unimodality with histograms. For all analytes, the individual results and ampoule averages followed an approximately normal and unimodal distribution, with the exception of the individual values for ammonium, for which a bimodal distribution could be observed. This minor deviation from unimodality does not significantly affect the estimate of the between-unit standard deviation. Also for calcium the distribution of the ampoules averages looks bimodal, but the fact that the range of data is covered by $\pm 2s_{bb}$ gives enough confidence about the appropriateness of applying ANOVA.

Data were checked for presence of trends and outliers.

For potassium, a trend in the filling sequence towards higher values was found (at both 95 % and 99 % confidence levels).

Outlying samples averages were detected for potassium and sulfate (2 ampoules, Grubbs double test at $\alpha=0.05$), for conductivity (2 ampoules, Grubbs double test at $\alpha=0.05$ and $\alpha=0.01$) and for *ortho*-phosphate (1 unit, Grubbs single test at $\alpha=0.05$).

Since there were no technical reasons for the outlying results, all data were retained for statistical analysis. In this case, the evaluation by ANOVA could be not the most appropriate one and therefore an alternative approach for the estimation of the heterogeneity was followed (see formula 4 below).

The ANOVA allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the following formulas:

$$s_{wb} = \sqrt{MS_{within}} \quad (1)$$

MS_{within} = mean squares within-ampoule

s_{wb} is equivalent to the s of the method, provided that subsamples are representative for the whole bottle.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (2)$$

MS_{between} = mean squares between-ampoule
 n = number of replicates per ampoule.

When MS_{between} is smaller than MS_{within} , s_{bb} can not be calculated. Instead, u_{bb}^* , the heterogeneity that can be hidden by the method repeatability, is calculated, according to the following expression [9]:

$$u_{\text{bb}}^* = \frac{s_{\text{wb}}}{\sqrt{n}} \sqrt{\frac{2}{v_{MS_{\text{within}}}}} \quad (3)$$

$v_{MS_{\text{within}}}$ = degrees of freedom of MS_{within}

For potassium, sulfate, conductivity and *ortho*-phosphate, for which outlying bottle means were detected, an alternative estimate of heterogeneity was calculated. Between-bottle heterogeneity was modelled as rectangular distribution limited by the most extreme outlying average. The uncertainty using these outliers (u_{rect}) was then estimated as

$$u_{\text{rect}} = \frac{|\text{largest outlier} - \bar{y}|}{\sqrt{3}} \quad (4)$$

\bar{y} = average of all results

For potassium, for which a trend in the filling sequence was detected as well, the between-bottle heterogeneity was modelled using the half-width of a rectangular distribution between the highest and lowest bottle average.

$$u_{\text{rect}} = \frac{|\text{highest result} - \text{lowest result}|}{2 \cdot \sqrt{3}} \quad (5)$$

For the parameters for which ANOVA was applied, the larger value between s_{bb} and u_{bb}^* is taken as uncertainty contribution for homogeneity, u_{bb} . u_{rect} will be taken as u_{bb} for *ortho*-phosphate, potassium, sulfate and conductivity (Table 2).

With some exceptions, the between-unit variation is generally below 2 %. Exceptions are potassium and sodium, showing an uncertainty of homogeneity around 8-10 % and pH and conductivity for which $u_{\text{bb,rel}}$ is around 4 %.

Table 2. Results of the homogeneity study

	Mean value	unit	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$u_{rect,rel}$ [%]	$u_{bb,rel}$ [%]
ammonium	0.950	mg/L	0.1	0.6	0.1	-	0.6
calcium	0.274	mg/L	1.5	1.7	0.7	-	1.7
chloride	1.72	mg/L	0.3	0.7	0.1	-	0.7
fluoride	0.187	mg/L	1.1	0.6	0.5	-	0.6
magnesium	0.149	mg/L	0.7	1.1	0.3	-	1.1
nitrate	1.93	mg/L	0.8	1.6	0.4	-	1.6
<i>ortho</i> -phosphate	1.008	mg/L	-	-	-	2.0	2.0
potassium	0.244	mg/L	-	-	-	9.7 ¹	9.7
sodium	1.725	mg/L	0.3	7.6	0.1	-	7.6
sulfate	1.38	mg/L	-	-	-	0.8	0.8
pH (20 °C)	6.30	-	1.0	4.1	0.5	-	4.1
conductivity (20 °C)	18.1	μS/cm	-	-	-	4.3	4.3

¹for potassium two different u_{rect} were calculated, one related to the filling trend and the other related to the presence of outliers, in table is reported the largest value (linked to the presence of outliers).

For potassium and sodium a quite large scattering of the data is clearly visible. This could be due to a possible instability of these parameters caused by the uncontrolled released from the walls of the borosilicate ampoules used as container. The stability data (see below) also give a confirmation of such a suspicion. For pH and conductivity, an uncertainty related to homogeneity of around 4 % was considered as an acceptable contribution to the total uncertainty of the certified value. All homogeneity data can be found in Annex 1a and 1b.

6. Minimum sample intake

The minimum sample intake, *i.e.* the minimum subsample representative of the whole ampoule, was not specifically addressed due to the nature of the material itself (water). The heterogeneity of solutions is known to be very small or even negligible.

Nevertheless, minimum sample intake is defined as the smallest amount of sample for which homogeneity has been demonstrated through the obtainment of a technically valid set of results accepted for the characterisation. These amounts are the following: 0.005 mL for chloride, fluoride, nitrate and sulfate, 0.1 mL for ammonium, magnesium and *ortho*-phosphate and 10 mL for pH and conductivity.

7. Stability studies

7.1 Set-up of stability studies

Stability studies are conducted to establish both dispatch conditions (short-term stability) as well as storage conditions (long-term stability).

Principal means of stabilization of the water for long-term perspective were the creation of an inert atmosphere by flushing argon within the ampoule just before filling and the sterilization by exposing the ampoules to an autoclaving process (see Section 4.2).

For performing the stability studies according to the planned tested temperatures and time points, 28 ampoules were required for the short-term stability (14 for pH and conductivity and 14 for the rest of parameters) and 16 ampoules were required each of the long-term stability schemes, see below (8 for pH and conductivity and 8 for the rest of parameters), selected by random stratified sampling from the entire batch produced.

The set-up of the studies followed an isochronous scheme [10] as described below:

- Short-term stability

Two ampoules were kept at +18 °C and +60 °C for 1, 2 and 4 weeks, respectively, after which they were put at +4 °C, the temperature at which the "reference" ampoules were stored. Two replicate analyses per ampoule were performed under repeatability conditions *i.e.*, all analyses were included in the same analytical run according to a prescribed randomly selected sequence.

- Long-term stability

Two ampoules were kept at +18 °C for 4, 8, and 12 months, respectively (1st scheme) and for 8, 16 and 24 months, respectively (2nd scheme). The reference temperature was +4 °C. Three replicates per ampoule were performed under repeatability conditions.

The measurements were performed by photometry for ammonium and *ortho*-phosphate, by ICP-OES for calcium, magnesium, potassium and sodium, by IC-CD for chloride, fluoride, nitrate and sulfate, by potentiometry for pH and by conductimetry for conductivity (results reported at 20 °C), using standardised and in-house validated methods.

7.2 Results of stability studies

The results were grouped and evaluated for each time point and temperature. Results were screened for single and double outliers by applying the Grubbs test at confidence levels of 95 % and 99 %, respectively. Data were plotted against time and the regression lines were

calculated to check for significant trends possibly indicating degradation of the material. The observed slopes were tested for significance using a t -test, with $t_{\alpha,df}$ being the critical t -value (two-tailed) for a significance level $\alpha = 0.05$ (95 % confidence interval). The results for the short-term stability are summarised in Table 3.

Table 3. Short-term stability

	18 °C			60 °C		
	outliers	slope significance	$u_{\text{sts,rel}}[\%]$ /week	outliers	slope significance	$u_{\text{sts,rel}}[\%]$ /week
ammonium	-	no	0.1	unit 474 (DT, 95 and 99 %)	Yes (95 and 99 %)	0.1*
calcium	-	Yes (95 %)	0.6*	-	no	0.5
chloride	-	no	0.2	-	no	0.1
fluoride	unit 982 (DT, 95 and 99 %)	no	1.1	-	no	0.2
magnesium	-	no	0.3	-	no	0.3
nitrate	unit 526 (DT, 95 and 99 %)	no	0.5	unit 474 (DT, 95 %)	Yes (95 %)	0.4*
ortho-phosphate	-	no	0.2	-	Yes (95 and 99 %)	0.5*
potassium	-	no	1.8	-	no	1.3
sodium	-	no	2.1	unit 632 (DT, 95 %)	no	1.4
sulfate	-	no	0.2	-	no	0.2
pH (20 °C)	-	no	1.1	-	no	0.8
conductivity (20 °C)	-	Yes (95 %)	1.0*	-	no	0.6

* including trend (u_{sts} includes additional contribution given by the slope of the regression line)

DT = double Grubbs test

In all cases where outliers were observed, these were both results from the replicate measurements. Outliers occurred at either 18 °C or 60 °C. For nitrate outliers were observed at both temperatures but concerning two different units. No technical reason for exclusion of the outliers could be found, therefore they were retained leading to a conservative estimate of the short-term stability uncertainty. The resulting uncertainty contributions for short-term stability were calculated according to Linsinger *et al.* [11] and were found to be small or negligible (if compared to the uncertainty of the final assigned value) for almost all analytes (maximum 1.1 %). They will therefore not be considered in the uncertainty budget of the final

certified values. Exceptions are potassium and sodium for which the short-term uncertainty at 18 °C is about 2 %, but, also for this reason, for these two parameters no certified value will be assigned.

Significant slopes were observed for calcium and conductivity results at 18 °C at 95 % confidence interval but this finding was not confirmed by the 60 °C results and was thus considered as analytical artefact. Significant slopes were also found for ammonium, *ortho*-phosphate (both 95 and 99 % confidence interval) and nitrate (95 % confidence interval) at 60 °C. Following these results, in order to avoid possible degradation during dispatch, it was concluded that the transport of the material will occur under cooled conditions.

The results of the two long-term stability studies at +18 °C (1st scheme lasting 12 months and 2nd scheme lasting 24 months) were combined and evaluated together to obtain more confidence about the assessment of the stability, with the exception of pH, chloride and nitrate.

For pH only the 2-years study measurements were used. In the case of chloride and nitrate, it was decided to base the shelf-life on the measurements of the 1-year long-term stability study, because of doubtfulness of validity of the measurements belonging to one single ampoule (see below for more details).

Since the two datasets (1st scheme and 2nd scheme) were obtained from different laboratories and at different points in time, a correction had to be applied. For all parameters, the correction factor was between 0.90 and 1.11. The results are summarised in Table 4 (graphical depictions of the data can be found in Annex 2). The uncertainty due to storage at 18 °C is estimated for a shelf-life of 2 years.

The uncertainty of stability u_{ts} of the materials was calculated as uncertainty of the slope of the regression line multiplied with the chosen shelf life [11]:

$$u_{ts} = \frac{s}{\sqrt{\sum (x_i - \bar{x})^2}} t_{sl} \quad (6)$$

with s being the standard deviation of all 48 individual results of the stability studies (with the exception of chloride, nitrate and pH for which only 24 independent measurements were used), x_i being the time point for each replicate, \bar{x} being the average of all time points and t_{sl} being the pre-defined shelf life (24 months in this case).

Table 4. Long-term stability

	18 °C		
	outliers	slope significance	$u_{\text{ITS,rel}}$ [%] (2 years)
ammonium	-	no	0.5
calcium	-	no	1.1
chloride	-	no	1.1*
fluoride	-	no	0.5
magnesium	-	no	0.7
nitrate	One (ST, 95 %)	no	1.1*
<i>ortho</i> -phosphate	Two (DT, 95 %)	no	0.4
potassium	One (DT, 95 %)	no	3.2
sodium	-	Yes (95 and 99 %)	10.4**
sulfate	-	no	0.4
pH (20 °C)	-	no	0.5***
conductivity (20 °C)	-	no	1.4

* estimated based on the 1 year long term stability data

** including trend (u_{ITS} includes additional contribution given by the slope of the regression line)

***estimated using only the 2 years long term stability data

ST = single Grubbs test

DT = double Grubbs test

One outlier (individual result) was detected for potassium and nitrate, respectively, and two outliers from the same ampoule were identified for *ortho*-phosphate. These outliers were all kept for the statistical evaluation, in absence of any technical reason justifying the rejection. A tentative removal of the outliers for potassium, nitrate and *ortho*-phosphate did not result in a significant trend of the data, which means that the estimate of u_{ITS} is conservative.

A significant positive trend could be observed for sodium (both at a 95 and 99 % significance level). A possible reason for this could be the release of this element from the borosilicate glass of the ampoule.

Including this trend, the high uncertainty contribution of the long-term storage casts serious doubts about stability for sodium. Also for potassium a quite high uncertainty was calculated, confirming the scattering of data already observed in the homogeneity study. Therefore it was decided not to certify the mass concentration of these elements.

For pH the u_{ITS} was estimated using only the measurements of the 2nd scheme long term stability lasting 2 years. The reason for it relies on the fact that some doubts arose concerning

the validity of the data of the 1st scheme, underpinned by the failure of the involved laboratory in measuring pH in the QC samples sent along with the characterisation ampoules.

For chloride and nitrate, a significant slope became apparent after combination of the 1-year and 2-years stability data, while when using only the 1-year measurements no trend could be observed. The slope significance is caused by high values of the measurements of one single ampoule (n. 668), casting doubts on the actual occurrence of this trend. No conclusions could be drawn and it was decided to repeat the 2-years long term stability study measurements of chloride and nitrate sending for analysis the reserve set of samples dedicated to this scope.

This additional set of data will hopefully serve in clarifying the picture about the stability of these two parameters, possibly revising the shelf-life presently calculated from the 1-year stability data.

Summarising, because of the doubtfulness on the long-term stability (given by the significance of the slope and/or large u_{ls}) and also considering the outcome of the homogeneity study, sodium and potassium will not be further considered in the evaluation for the assignment of certified values.

For the rest of analytes, the uncertainty introduced by the long-term stability at +18 °C (storage temperature of the material) for 2 years is well below 2 %. u_{ls} is taken up in the final uncertainty of the certified value. The shelf life of the material will be re-evaluated in the future, based on the results of the stability monitoring carried out after certification and release of the material.

8. Characterisation

8.1 Study design

The characterisation of the material was carried out by an intercomparison exercise and finalised in 2009. Laboratories were selected on the basis of expertise in water analysis (with supporting documentation on their measurement capabilities), quality requirements criteria (e.g. successful participation in intercomparisons in the relevant field and/or previous characterisation exercises), with accreditation in the specific analysis to be performed considered as an asset. Laboratories were only allowed to use validated methods.

Most participating laboratories were accredited to ISO 17025, and where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (see Section 2).

In order to prevent biased results, a number of precautionary measures were taken:

- when possible, completely different and independent analytical methodologies were chosen for the determination of the same parameter (still aiming to at least 2 laboratories per method), thus being able to demonstrate the absence of method bias.
- six independent measurements per laboratory were required, meaning that a new sample preparation had to be performed for each measurement. These measurements were prescribed to be spread over two days, to ensure within-laboratory reproducibility conditions.
- to further demonstrate the accuracy and traceability of their data, laboratories were asked to report results of quality control samples analysed together with the characterization samples and were asked to insert blanks in the measuring sequence.
- samples for the characterisation study covered the whole batch produced and were selected using a random stratified sampling scheme.

The two quality control samples received by the laboratories were the certified reference materials BCR-408 (re-labelled as QC3) and BCR-409 (re-labelled as QC4), "Simulated rainwater (low content)" and " Simulated rainwater (high content)", respectively.

Laboratories were also asked to provide an estimate of the measurement uncertainty and to describe the approach used to derive the uncertainty budget.

Depending on the methodology employed (and the relative sample intake), laboratories received 6 (3 for pH and conductivity measurements and 3 for the rest of analytes) or 4 (2 for pH and conductivity measurements and 2 for the rest of analytes) ampoules of the candidate certified reference material ERM-CA408: six independent results were to be returned. Additionally they received two ampoules of quality control samples, as explained before: only two replicates were asked in this case (only one measurement was required for pH and conductivity due to the relatively large sample intake needed for these measurements).

For helping the laboratories in establishing the correct calibration curve, in the guidelines for characterisation measurements an approximate concentration range for the parameters to be analysed was provided.

8.2 Data evaluation and results

A detailed overview of the analytical techniques used by the laboratories for the characterisation of ERM-CA408 is presented in Annex 3, listed per parameter.

Upon receipt of the datasets, the results were subject to technical evaluation. The results of the QC samples could be directly used to check for absence of significant bias.

Datasets were rejected whenever the laboratory reported a technical problem, when one or both quality control samples results did not agree with the certified values (according to ERM Application Note 1 [13]) and/or the RSD of the measurement results reported for ERM-CA408 exceeded 10 % (quality criterion set considering the required trueness asked in the technical specifications of the characterisation study and the repeatability claimed by the laboratories). A summary of the data evaluation is presented in Table 5. Small letters are added to the tags of laboratories reporting results with two different techniques.

The following datasets were discarded:

L0: measurement results of pH discarded because the result from QC3 did not agree with the certified value.

L1: measurement results of magnesium, nitrate and conductivity rejected because the RSD of the results were 14.5, 14.4 and 11.6 %, respectively; measurements of sulfate rejected because of inadequate limit of quantification.

L2: measurement results of ammonium rejected because the result from QC4 did not agree with the certified value; measurement results of calcium rejected because RSD exceeding quality criterion (11.1 %).

L3: measurement results of magnesium rejected because the RSD of the results was 14.1 % and because the result from QC4 did not agree with the certified value; measurement results of sulfate rejected because the results of both QC3 and QC4 did not agree with the certified values; measurements of conductivity rejected because of too high RSD (35.9 %); measurement results of *ortho*-phosphate excluded because the laboratory determined total phosphorus.

L4: measurement results of pH and conductivity were discarded as a consequence of reported problems with the washing of the electrodes between replicates (the three results were obtained from the same aliquot of water, not in compliance with the guidelines requesting for three independent measurements)

L7: their measurement results were all discarded because the laboratory failed in analysing many values (35 % of the total) of the QCs samples demonstrating lack of accuracy (the results of ammonium in QC4 did not agree with the certified value; the results of chloride and sulfate of both QCs samples did not agree with the certified values; the results of magnesium showed a RSD equal to 18.4 %).

L8: measurement results of sulfate rejected because the results reported for QC3 did not agree with the certified values.

L9: measurement results of chloride and nitrate rejected because the results reported for QC4 and QC3, respectively, did not agree with the certified values.

L10: measurement results of nitrate rejected because the value reported for QC3 did not agree with the certified value.

L11: measurement results of chloride discarded because of too high RSD (35.1 %) and measurement results of sulfate discarded because the result of QC3 did not agree with the certified value.

After this technical scrutiny, all the remaining datasets were accepted for further statistical assessment. Nine datasets from as many laboratories were accepted for fluoride, 9 datasets from 8 laboratories were accepted for *ortho*-phosphate, 8 datasets from 7 laboratories were accepted for nitrate, 8 datasets from as many laboratories were accepted for ammonium, calcium, chloride and pH, 7 datasets from as many laboratories were accepted for magnesium and conductivity, 6 datasets from as many laboratories were accepted for sulfate.

Table 5. Summary of the technical evaluation

	ammonium	calcium	chloride	fluoride	magnesium	nitrate	ortho-phosphate	sulfate	pH	conductivity.
L0									Discarded QC3 out	
L1(a)					Discarded RSD 14.5 %	Discarded RSD 14.4 %		Discarded LOQ about 1 mg/L		Discarded RSD 11.6 %
L2	Discarded QC4 out	Discarded RSD 11.1 %								
L3					Discarded QC4 out and RSD 14.1 %		Discarded Determination of total P	Discarded QCs out		Discarded RSD 35.9 %
L4									Discarded Reported problems in washing the electrodes, 3 consecutive measurements. on the same aliquot	Discarded Reported problems in washing the electrodes, 3 consecutive measurements. on the same aliquot
L5										
L6	-		-	-	-	-	-	-		
L7	Discarded QC4 out		Discarded QCs out		Discarded RSD 18.4 %			Discarded QCs out		
L8(a)								Discarded QC3 out		
L9			Discarded QC4 out			Discarded QC3 out				
L10						Discarded QC3 out				
L1b	-	-	Discarded RSD 35.1 %	-	-			Discarded QC3 out		-
L8b	-	-	-	-	-		-	-		-

- parameter not analysed

The datasets accepted on technical grounds were tested for outlying laboratories using Dixon, Grubbs and Nalimov t -test, for normality of means distribution using kurtosis/skewness tests and for outlying variances using Cochran test.

Table 6 shows a summary of the statistical analysis for ERM-CA408, where s stands for standard deviation of the laboratories' means.

Table 6. Statistical evaluation of technically accepted datasets

	number of individual data	outlier means	normality	s	unit
ammonium	48	-	yes	0.03	mg/L
calcium	48	L5	yes (99 %)	0.071	mg/L
chloride	48	-	yes	0.06	mg/L
fluoride	54	-	yes	0.010	mg/L
magnesium	42	L2	yes	0.014	mg/L
nitrate	47	-	yes	0.03	mg/L
<i>ortho</i> -phosphate	54	-	yes	0.03	mg/L
sulfate	36	-	n.a.*	0.04	mg/L
pH (20 °C)	48	-	yes	0.234	-
conductivity (20 °C)	42	L2	yes	0.7	μS/cm

* too few datasets for a meaningful outcome

L5 was identified as outlier for calcium. No technical issue could be indicated for excluding the result. Considering the measurement uncertainty reported by the laboratory, the measured value is significantly different from the certified value, hence it was decided not to assign any certified value for calcium and this parameter will not be further considered in the evaluation. L2 was identified as outlier for magnesium and conductivity, but no technical reason could be found for excluding the results. For conductivity, considering the associated measurement uncertainty reported by the concerned laboratory, the measured value is not significantly different from the certified value. For magnesium the measurement uncertainty reported by this laboratory is touching the uncertainty associated to the certified value, but not overlapping. For this reason, it was decided to increase the uncertainty of the certified value to an extent that the result of laboratory 2 fulfils the condition of ERM Application Note 1 [13]. As a consequence, the results of laboratory L2 were included in the calculation of the mean and uncertainty of characterization (u_{char}).

All datasets follow normal distributions. Average and standard deviations are therefore meaningful estimators for the expected value and its variation.

In Table 7 the characterisation results of the simulated rainwater material, expressed as the mean of means of the accepted datasets, are presented. The relative standard error of the mean of means is used as an estimation of the uncertainty contribution of the characterisation exercise ($u_{\text{char,rel}}$).

Table 7. Characterisation results

	Mean of means	unit	p	$\text{RSD}_{\text{average}} [\%]$	$\text{RSE}_{\text{average}} [\%]$ $u_{\text{char,rel}}$
ammonium	0.91	mg/L	8	3.6	1.3
chloride	1.96	mg/L	8	2.8	1.0
fluoride	0.194	mg/L	9	5.1	1.7
magnesium	0.145	mg/L	7	9.7	3.7
nitrate	2.01	mg/L	8	1.6	0.6
<i>ortho</i> -phosphate	1.00	mg/L	9	2.6	0.9
sulfate	1.46	mg/L	6	2.6	1.0
pH (20 °C)	6.3	-	8	3.9	1.4
conductivity (20 °C)	18.7	$\mu\text{S/cm}$	7	3.7	1.4

9 Certified values and uncertainties

The certified values of the simulated rainwater ERM-CA408 were calculated as the unweighted mean of the means of the accepted datasets (see Table 7).

The relative combined uncertainty of the certified values of the CRM consists of uncertainties related to characterisation (u_{char}), between bottle heterogeneity (u_{bb}) and long-term storage (u_{its}) [12].

- u_{char} was estimated as the standard deviation of the mean of laboratory means, i.e. s/\sqrt{p} with s and p taken from Table 6 and Table 7.
- u_{bb} was estimated as s_{bb} , standard deviation between-units (for all certified parameters larger than u^*_{bb} , maximum heterogeneity potentially hidden by method repeatability) or as u_{rect} in the case of *ortho*-phosphate, potassium, sulfate and conductivity (see Table 2).
- u_{its} was mostly estimated combining the 1 year and 2 years long-term stability results at 18 °C projected for a time frame of 2 years (with exception of chloride and nitrate, for which

only the 1 year data were used and pH for which only the 2 years data were used) (see Table 3).

These uncertainties were combined quadratically to estimate the relative combined uncertainty of the certified value $u_{CRM,rel}$ according to:

$$u_{CRM,rel} = \sqrt{u_{bb,rel}^2 + u_{lts,rel}^2 + u_{char,rel}^2} \quad (7)$$

The relative expanded uncertainty $U_{CRM,rel}$ is given by the following expression, where $k = 2$ is chosen as coverage factor to provide a confidence level of approximately 95 %:

$$U_{CRM,rel} = k \cdot u_{CRM,rel} \quad (8)$$

The absolute expanded uncertainty U_{CRM} is then calculated by rounding up the value obtained multiplying the certified value with the relative expanded uncertainty $U_{CRM,rel}$.

The absolute expanded uncertainty of the certified value for magnesium, calculated as 0.012 mg/L, will be increased to 0.022 mg/L, in such a way that the result of laboratory 2 fulfils the condition of ERM Application Note 1 [13] (see Annex 4 for more details).

The various uncertainty contributions, the expanded uncertainties and the certified values are summarised in Table 8.

Table 8. Certified values and uncertainty budget for ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate, pH and conductivity in ERM-CA408

	$u_{bb,rel}$ [%]	$u_{lts,rel}$ [%]	$u_{char,rel}$ [%]	$U_{CRM,rel}$ ($k=2$) [%]	Certified value	U_{CRM} ($k=2$)	unit
ammonium	0.6	0.5	1.3	3.0	0.910	0.028	mg/L
chloride	0.7	1.1	1.0	3.3	1.96	0.07	mg/L
fluoride	0.6	0.5	1.7	3.7	0.194	0.008	mg/L
magnesium	1.1	0.7	3.7	7.8	0.145	0.022*	mg/L
nitrate	1.6	1.1	0.6	4.1	2.01	0.09	mg/L
<i>ortho</i> -phosphate	2.0	0.4	0.9	4.5	1.00	0.05	mg/L
sulfate	0.8	0.4	1.0	2.7	1.46	0.04	mg/L
pH (20 °C)	4.1	0.5	1.4	8.7	6.3	0.6	-
conductivity (20 °C)	4.3	1.4	1.4	9.5	18.7	1.8	μS/cm

*increased to an extent that the result of laboratory 2 fulfils the condition laid down in ERM Application Note 1.

Annex 4 summarises the result of the characterisation exercise and presents as well a graphical depiction of the assigned values, together with averages and standard deviations of the individual laboratories for ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate, pH and conductivity with the participating laboratories encrypted by codes (L0 to L10).

10 Metrological traceability

Laboratories quantified the analytes using different and independent analytical methodologies, both regarding sample preparation as well as measurement principles, with the exception of chloride and sulfate (for which only IC-CD was used), pH and conductivity. The calibrants employed were either commercially available, in-house gravimetrically prepared or CRMs, all traceable to the SI. For ammonium, fluoride, magnesium, nitrate and *ortho*-phosphate, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes. In the absence of results from other analytical methods confirming the absence of method bias, chloride and sulfate will be classified as operationally defined measurands (as obtained by IC-CD).

Only validated methods were used. Agreement with the certified values of the quality control materials further proved absence of significant bias, correctness of the calibration curves and proper calibration of all relevant input parameters.

The realisation of the above-mentioned conditions demonstrates that the certified values are traceable to the International System of Units (SI).

11 Commutability

ERM-CA408 is a simulated rainwater, obtained by dissolution of high quality chemicals in ultra-pure water. The laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding sample preparation, calibration and detection. The agreement between the results obtained, leading to the certification of several parameters, shows that ERM-CA408 exhibits the same behaviour as a typical laboratory sample and confirms its commutability.

12 Instructions for use

12.1 Storage conditions

The material shall be stored at $+18\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ in the dark. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of open samples.

12.2 Minimum sample intake

The minimum amount of sample to be used is 0.005 mL for chloride, fluoride, nitrate and sulfate, 0.1 mL for ammonium, magnesium and *ortho*-phosphate and 10 mL for pH and conductivity.

12.3 Safety precautions

The usual laboratory safety measures apply.

12.4 Intended use

ERM-CA408 is intended for method validation and quality control purposes. Samples should be allowed to equilibrate to room temperature (20 -25 °C) before use.

12.5 Use of the certified value

For assessing the trueness of an analytical method, the CRM is analysed by the laboratory and the result is compared to the certified value as described in ERM Application Note 1 [13].

A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result:

- Calculate the absolute difference between the mean of the CRM measurement results and the certified value (Δ_m).
- Convert the expanded uncertainty of the certified value U_{CRM} into a standard uncertainty (u_{CRM}) by dividing U_{CRM} with the coverage factor $k=2$.
- Combine the standard uncertainty of the measurement result (u_m) with the uncertainty of the certified value (u_{CRM}) as follows:

$$u_{\Delta} = \sqrt{u_m^2 + u_{CRM}^2} \quad (9)$$

If $\Delta_m < 2 \cdot u_{\Delta}$, there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

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Annex 1a

Homogeneity data for ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate and sulfate in ERM-CA408 expressed as mg/L

Ampoule number	Ammonium		Calcium		Chloride		Fluoride		Magnesium		Nitrate		<i>Ortho</i> -phosphate	
	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2
31	0.951	0.953	0.2624	0.2714	1.71	1.71	0.1887	0.1846	0.146	0.145	1.93	1.97	0.977	0.970
137	0.953	0.956	0.2772	0.2779	1.71	1.71	0.1869	0.1890	0.152	0.149	1.95	1.97	1.029	1.028
304	0.955	0.954	0.2806	0.2765	1.72	1.72	0.1861	0.1856	0.150	0.149	1.90	1.90	1.010	1.037
410	0.955	0.956	0.2798	0.276	1.72	1.73	0.1863	0.1881	0.151	0.151	1.94	1.97	1.009	0.982
560	0.946	0.946	0.2678	0.2649	1.73	1.74	0.1893	0.1924	0.148	0.147	1.90	1.92	1.006	1.013
690	0.952	0.952	0.2834	0.2719	1.73	1.72	0.1886	0.1874	0.148	0.149	2.00	1.98	0.994	1.022
822	0.945	0.945	0.2800	0.2719	1.74	1.74	0.1853	0.1885	0.150	0.149	1.92	1.93	1.017	1.011
971	0.956	0.959	0.2719	0.2667	1.73	1.73	0.1862	0.1873	0.149	0.148	1.91	1.91	1.013	1.010
1116	0.946	0.948	0.2792	0.2787	1.71	1.70	0.1856	0.1822	0.150	0.152	1.88	1.90	1.002	0.997
1246	0.941	0.940	0.2683	0.2662	1.73	1.74	0.1831	0.1885	0.151	0.151	1.91	1.90	1.010	1.023

Annex 1a (continued)

Ampoule number	Potassium		Sodium		Sulfate	
	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2
31	0.211	0.211	1.943	1.944	1.40	1.40
137	0.203	0.202	1.677	1.678	1.39	1.36
304	0.249	0.245	1.739	1.738	1.38	1.39
410	0.238	0.237	1.604	1.601	1.38	1.38
560	0.256	0.253	1.791	1.784	1.39	1.38
690	0.255	0.255	1.885	1.879	1.41	1.40
822	0.272	0.226	1.521	1.502	1.38	1.38
971	0.272	0.267	1.792	1.791	1.39	1.38
1116	0.269	0.262	1.661	1.664	1.37	1.38
1246	0.254	0.25	1.653	1.648	1.38	1.37

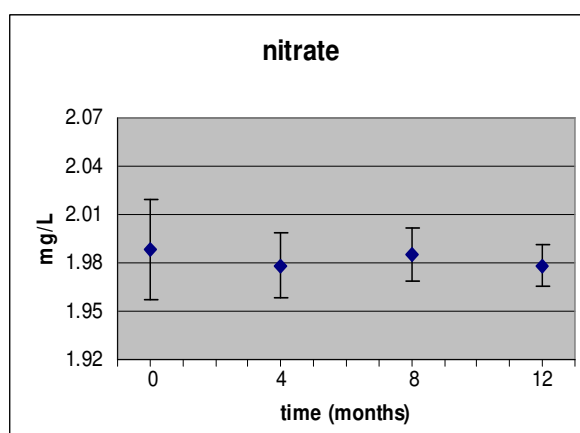
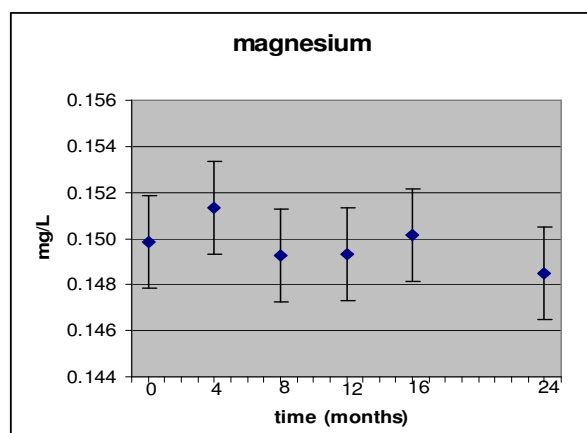
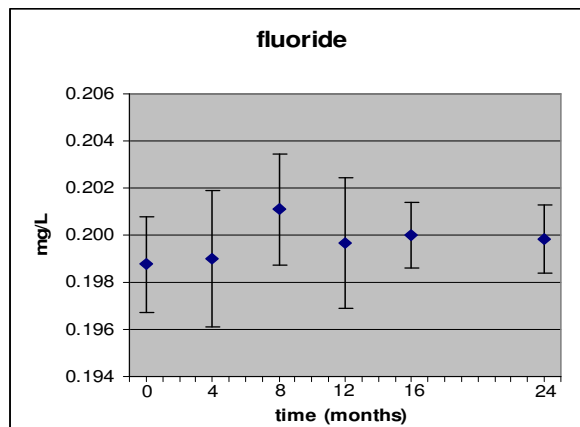
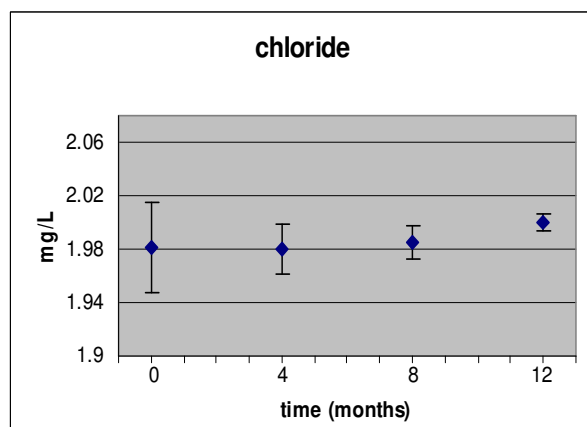
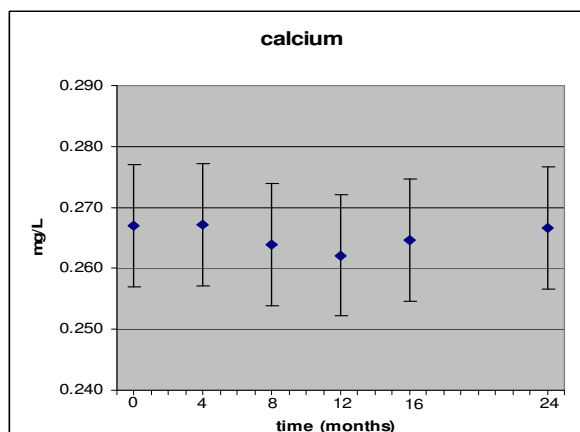
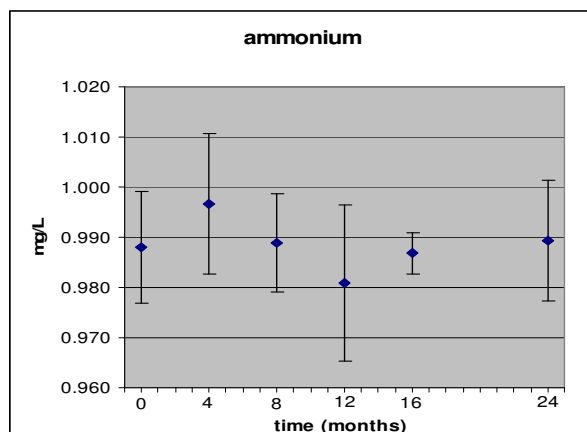
Annex 1b

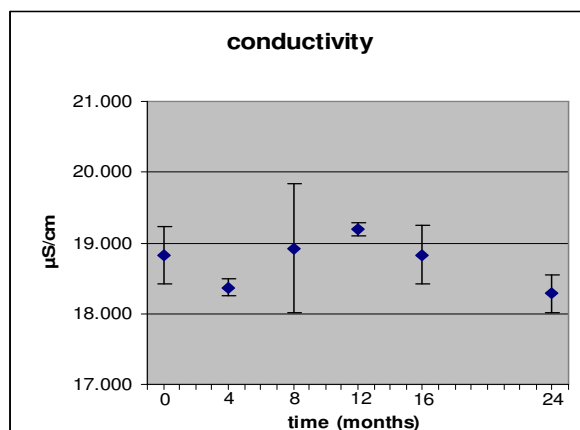
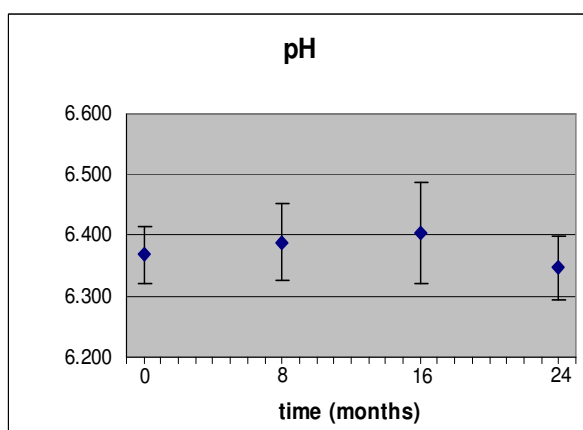
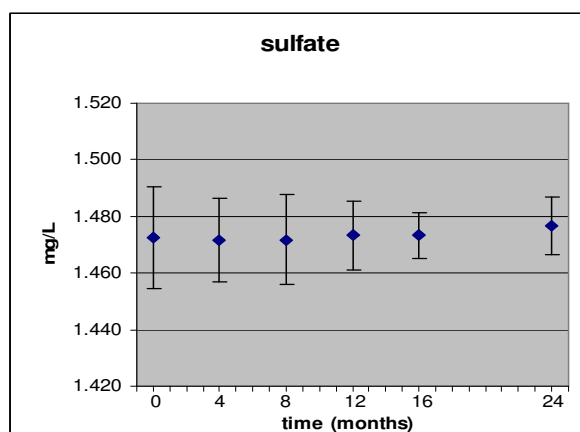
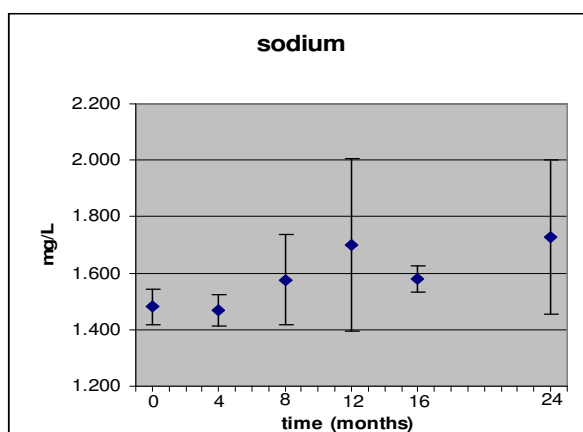
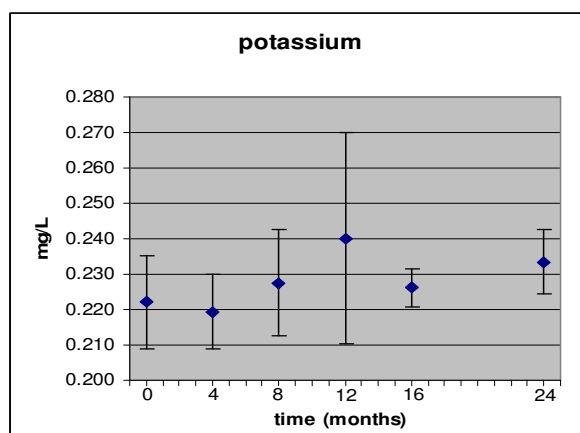
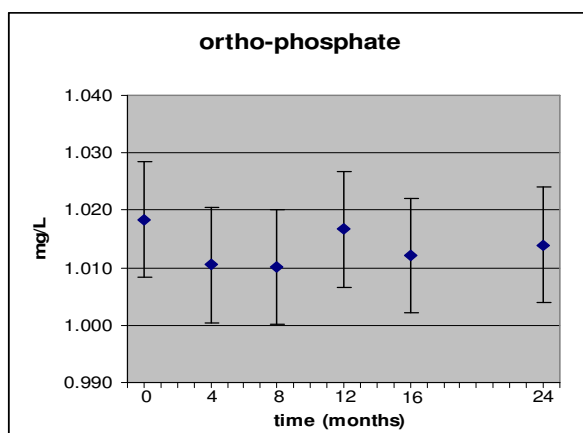
Homogeneity data for pH and conductivity in ERM-CA408

Ampoule number	pH		Conductivity [μS/cm]	
	replic.1	replic.2	replic.1	replic.2
94	6.79	6.59	19.4	19.6
211	6.27	6.35	17.9	17.9
365	6.13	6.11	17.7	17.9
492	6.71	6.75	19.3	19
634	6.14	6.04	17.9	17.8
775	6.11	6.14	17.7	17.7
905	6.27	6.23	17.9	17.9
1036	5.95	5.88	17.4	17.5
1175	6.30	6.27	17.9	17.9
1319	6.44	6.54	18.3	18.3

Annex 2: Graphical depictions of long-term stability data for ammonium, calcium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, potassium, sodium, sulfate, pH and conductivity in ERM-CA408

The graphs report ampoule averages per time point and their 95 % confidence intervals based on the standard deviations of the replicates per time (12 for points 0 and 8 months, 6 for points 4, 12, 16 and 24 months). The uncertainty bars of the chloride nitrate and pH measurements represent the 95 % confidence intervals based on the standard deviations of 6 replicates per time point.





Annex 3. Detailed description of the analytical techniques used in the characterization of ERM-CA408.
Small letters are added to the tags of laboratories when reporting results with two different techniques

Ammonium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	none	5	PHOT, CFA Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.01, 0.03, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8, 1.0 NH ₄ Cl	0.009
L1	none	~15	PHOT, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0, 0.1, 0.6, 1.2, 2 [N] Commercially available mixed standard	0.5[N]
L3	dilution	5	PHOT, 690 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.1, 0.2, 0.5 NH ₄ Cl	0.1
L4	none	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Quadratic 0.064, 0.13, 0.26, 0.51, 1.29, 2.58 NH ₄ Cl >99.99	0.09
L5	none	0.1	PHOT, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Polynomial (2 nd order) 0, 0.05, 0.1, 0.3, 0.6, 1.2, 2.0 Commercially available standard	0.02
L8	none	10	PHOT Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear, 8 points 0+ 0.01-0.8 [N] NH ₄ Cl	0.01[N]
L9	dilution	0.23	PHOT, SFA Modified Berthelot reaction	Linear 0.1, 0.2, 0.3, 0.4, 0.5 NH ₄ Cl solid p.a.	0.1
L10	Dilution 1:5	5	PHOT, batch photometry Reaction with salicylate and dichloroisocyanurate (indophenol method)	Linear 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 Commercially available standard, Certipur1000 mg/L	0.0182

Chloride

Lab	Sample pre-treatment	Sample intake (mL)	Analytical method and determination	Calibration: type, points (mg/L), calibrant	LOQ (mg/L)
L0	none	0.025	IC CD 25 µL injection volume, pre-column IonPac AG12, column IonPac AS12, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	quadratic 0.5, 1, 2, 4, 8, 12, 15 NaCl	0.32
L1	none	~15	IC CD 100 µL injection volume, pre-column IonPac AG9-HC, column IonPac AS9-HC, eluent: 10 mM Na ₂ CO ₃ , ASRS Ultra suppressor	quadratic 0.050, 0.100, 0.250, 0.500, 1.000, 2.000 Commercially available single element standard	0.05
L2	none	0.2	IC CD pre-column Dionex AG4, column Dionex AS4, eluent: carbonate/bicarbonate	External calibration 0.2, 0.5, 1, 3, 5 NaCl	0.2
L3	none	5	IC CD 25 µL injection volume, pre-column AG12A, column AS12A, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Linear 2.5*, 5, 10, 20 Commercially available Cl standard	0.5
L4	none	5	IC CD 100 µL injection volume, pre-column Dionex AG19, column Dionex AS19, eluent: 19 mM KOH, ASRS electrolytic suppressor	Linear 0.05, 0.1, 0.2, 0.5, 2, 5, 10 NaCl >99.99	0.06
L5	none	0.005	IC CD 5 µL injection volume, pre-column IonPac AG19, column IonPac AS19, EluGen Cartridge Potassium Hydroxide, ASRS ultra suppressor	Linear 5, 10, 25, 50, 125, 250 Commercially available standard	0.02
L8	none	3	IC CD guard column IonPac AG14A, column AS14A, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , ASRS Ultra II suppressor	Quadratic 1.0, 2.5, 5.0, 10 NaCl	3**
L10	none	0.1	IC CD 100 µL injection volume, guard column AG14, column AS14, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , autorecycle mode suppression	Linear 1.0, 2.0, 5.0, 10.0, Commercially available standard Certipur 1000 mg/L	0.401

*even though the lowest calibration point was above the measurement result, L3 ensured the correct quantification of the peak through their method validation study, in which linearity is proven starting at least from the LOQ.

**even though the stated LOQ is above the measurement result, L8 provided the related chromatograms as a proof that the peaks were clearly quantifiable.

Fluoride

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	none	0.025	IC CD 25 µL injection volume, pre-column IonPac AG12, column IonPac AS12, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Quadratic 0.05, 0.1, 0.2, 0.4, 0.8, 1.2, 1.5 NaF	0.034
L1	none	~15	IC CD 100 µL injection volume, pre-column IonPac AG9-HC, column IonPac AS9-HC, eluent: 10 mM Na ₂ CO ₃ , ASRS Ultra suppressor	Quadratic 0.050, 0.100, 0.250, 0.500, 1.000, 2.000 Commercially available single element standard	0.05
L2	Dilution in TISAB buffer (pH=5.8)	20	ISE	10 ⁻³ , 10 ⁻⁴ , 10 ⁻⁵ mol/L NaF	-
L3	none	20	ISE	0.1, 0.2, 0.3 Commercially available F standard	-
L4	none	5	IC CD 100 µL injection volume, pre-column Dionex AG19, column Dionex AS19, eluent: 19 mM KOH, ASRS electrolytic suppressor	Linear 0.1, 0.2, 0.3 commercial NaF solution	0.01
L5	none	0.005	IC CD 5 µL injection volume, pre-column IonPac AG19, column IonPac AS19, EluGen Cartridge Potassium Hydroxide, ASRS ultra suppressor	Linear 0.2, 0.4, 1, 2, 5, 10 Commercially available standard	0.02
L8	none	3	IC CD guard column IonPac AG14A, column AS14A, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , ASRS Ultra II suppressor	Quadratic 0.1, 0.2, 0.5, 1.0, 2.0 NaF	0.1
L9	none	2.1	PHOT Alizarin fluorineblue method	Linear 0, 0.2, 0.4, 0.6, 0.8, 1.0	0.2
L10	none	0.1	IC CD 100 µL injection volume, guard column AG14, column AS14, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , autorecycle mode suppression	Second order 0.01, 0.02, 0.05, 0.1, 0.25, 0.5, 1.0 Commercially available standard Certipur 1000 mg/L	0.0408

Magnesium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	Acidification with HNO ₃	4.95	ICP-OES	Linear 1, 10, 50, 100 Mg(NO ₃) ₂	0.084
L2	none	0.12	ICP-OES	Linear, 4 points incl. blank 0.1, 0.25, 0.5 Mg(NO ₃) ₂	0.05
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Linear 0.025, 0.05, 0.1, 0.3, 1, 2, 5 Mg(NO ₃) ₂ solution	0.03
L5	Acidification with HNO ₃	-	ICP-OES	Polynomial (2 nd order) 0, 5, 10, 20, 50, 100, 200 Commercially available magnesium standard	0.02
L8	none	2	ICP-OES	Linear 0, 5, 30 Commercially available magnesium standard	0.01
L9	none	10	ICP-OES	Two-points calibr. 0, 2.5 Mg(NO ₃) ₂ ·6H ₂ O	0.05
L10	Acidification with 2 % HNO ₃	5	ICP-OES	Linear 0.01, 0.02, 0.03, 0.04, 0.05, 0.08, 0.1, 0.5, 1.0 Commercially available standard 10 g/L	0.0049

Nitrate

Lab	Sample pre-treatment	Sample intake (mL)	Analytical method and determination	Calibration: type, points (mg/L), calibrant	LOQ (mg/L)
L0	none	1	IC CD 25 µL injection volume, pre-column IonPac AG12, column IonPac AS12, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Quadratic 0.5, 1, 2, 4, 8, 12, 15 NaNO ₃	0.32
L2	none	0.2	IC CD pre-column Dionex AG4, column Dionex AS4, eluent: carbonate/bicarbonate	External calibration 0.5, 1, 3, 5 NaNO ₃	0.2
L3	none	5	IC CD 25 µL injection volume, pre-column AG12A, column AS12A, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Linear 5, 10, 20, 40 Commercially available nitrate standard	0.5
L4	none	5	IC CD 100 µL injection volume, pre-column Dionex AG19, column Dionex AS19, eluent: 19 mM KOH, ASRS electrolytic suppressor	Linear 0.22, 0.44, 0.88, 2.21, 6.64, 13.28, 22.13 NaNO ₃ >99.99	0.09
L5	none	0.005	IC CD 5 µL injection volume, pre-column IonPac AG19, column IonPac AS19, EluGen Cartridge Potassium Hydroxide, ASRS ultra suppressor	Linear 5, 10, 25, 50, 125, 250 Commercially available standard	0.04
L8a	dilution	2	PHOT Reduction in presence of Cd at pH 8.5 and reaction with sulfanilamide	linear 0, 0.05, 0.100, 0.200 [N] KNO ₃	0.003[N]
L1b	none	15	IC CD 100 µL injection volume, guard column Ionpac AG9-HC, column AS9-HC, eluent: 10 mM Na ₂ CO ₃ , ASRS Ultra suppressor	Quadratic 0.050, 0.100, 0.250, 0.500, 1.000, 2.000 Commercially available single element standard	0.05
L8b	none	3	IC CD 50 µL injection volume, pre-column IonPac AG14A, column IonPac AS14A, eluent: 3.5 mM Na ₂ CO ₃ +1.0 mM NaHCO ₃ , ASRS Ultra II suppressor	Quadratic 0.25, 0.50, 1.0, 2.0, 5.0	0.2

*even though the lowest calibration point was above the measurement result, L3 ensured the correct quantification of the peak through their method validation study, in which linearity is proven starting at least from the LOQ.

Ortho-phosphate

Lab	Sample pre-treatment	Sample intake (mL)	Analytical method and determination	Calibration: type, points (mg/L), calibrant	LOQ (mg/L)
L0	dilution	5	PHOT Ammonium molybdate method	Linear 0.01, 0.03, 0.06, 0.12, 0.18, 0.24, 0.30, 0.36, 0.42 KH ₂ PO ₄	0.002
L1a	none	~15	PHOT, 880 nm Ammonium molybdate method	Linear 0, 12.5, 75, 150, 250 [P] Commercially available single element standard	0.01[P]
L2	dilution	10	PHOT Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	External calibration 0.00, 0.184, 0.307, 0.614, 1.228, 1.842, 2.456, 3.070 P ⁵⁺ in water (stabilised)	0.06
L4	dilution	~11	PHOT, 890 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0.012, 0.025, 0.04, 0.05, 0.09, 0.18, 0.31, 0.61, 1.23 KH ₂ PO ₄ 99,999 %	0.015
L5	none	0.1	PHOT, 880 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0, 0.1, 0.2, 0.5, 1, 1.5, 2, 2.57 Phosphate standard solution	0.04
L8	-	10	PHOT Ammonium molybdate method	Linear, 8 points 0+ 0.02-1.0 [P] KH ₂ PO ₄	0.005[P]
L9	none	0.6	PHOT, SFA, 880 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 [P] KH ₂ PO ₄	0.05[P]
L10	Dilution 1:5	10	PHOT, batch photometry Ammonium molybdate method	Linear 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 Commercially available standard, Certipur1000 mg/L	0.0858
L1b	none	~15	IC CD 100 µL injection volume, pre-column IonPac AG9-HC, column IonPac AS9-HC, eluent: 10 mM Na ₂ CO ₃ , ASRS Ultra suppressor	Quadratic 0.050, 0.100, 0.250, 0.500, 1.000, 2.000 Commercially available single element standard	0.01

Sulfate

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	none	0.025	IC CD 25 µL injection volume, pre-column IonPac AG12, column IonPac AS12, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Quadratic 0.5, 1, 2, 4, 8, 12, 15 Na ₂ SO ₄	0.26
L2	none	0.2	IC CD pre-column Dionex AG4, column Dionex AS4, eluent: carbonate/bicarbonate	External calibration 0.5, 1, 3, 5 Na ₂ SO ₄	0.2
L4	none	5	IC CD 100 µL injection volume, pre-column Dionex AG19, column Dionex AS19, eluent: 19 mM KOH, ASRS electrolytic suppressor	Linear 0.25, 0.5, 1, 2.5, 10, 25, 50 K ₂ SO ₄ 99.999	0.14
L5	none	0.005	IC CD 5 µL injection volume, pre-column IonPac AG19, column IonPac AS19, EluGen Cartridge Potassium Hydroxide, ASRS ultra suppressor	Linear 5, 10, 25, 50, 125, 250* Commercially available standard	0.04
L9	-	0.050	IC CD RP guard column, column Metrosepp A supp 7, ASRS suppressor	Quadratic 1, 2, 4, 6, 8, 10 Na ₂ SO ₄	1
L10	none	0.1	IC CD 100 µL injection volume, guard column AG14, column AS14, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , autorecycle mode suppression	Linear 1.0, 2.0, 5.0, 10.0 Commercially available standard Certipur 1000 mg/L	0.307

*even though the lowest calibration point was above the measurement result, L5 ensured the correct quantification of the peak through their method validation study, in which linearity is proven starting from the LOQ.

pH (at 20 °C)

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: calibrant, points</i>
L1	none	~40	potentiometry	Commercially available standards Buffers at pH 2.00, 4.01, 7.00, 10.00
L2	none	15	potentiometry	Commercially available standards Buffers at pH 2.00, 9.21
L3	none	20	potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 4.0, 7.0, 10.0
L5	none	15	potentiometry	Commercially available standards Buffers at pH 4.00 and 7.00
L6	none	~30	Potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 4.00 and 7.02
L8	none	10	Potentiometry measurements carried out at 20 °C	Commercially available stock solution Buffers at pH 7.00 and 10.00
L9	none	20	potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 4.00 and 7.02
L10	none	25	potentiometry	Commercially available standards Certipur Buffers at pH 6.88 and 9.22

Conductivity (at 20 °C)

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: calibrant, points</i>
L0	none	not stated	conductimetry measurements carried out @ 20 °C	KCl 0.01 M
L2	none	15	conductimetry	KCl 3 and 10 M
L5	none	15	conductimetry	Commercially available standard 1276 µS/cm
L6	none	~30	conductimetry measurements carried out @ 20 °C	Commercially available KCl solutions 18.06 µS/cm
L8	none	~10	conductimetry	Commercially available solution 1413 µS/cm
L9	none	20	conductimetry measurements carried out @ 20 °C	NaCl 0.05 m/m %
L10	none	25	conductimetry	Commercially available standards Certipur 0.147 mS (T=25 °C), 0.133 mS (T=20 °C)

Annex 4. Characterisation measurement results used in the certification of ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate, pH and conductivity in ERM-CA408

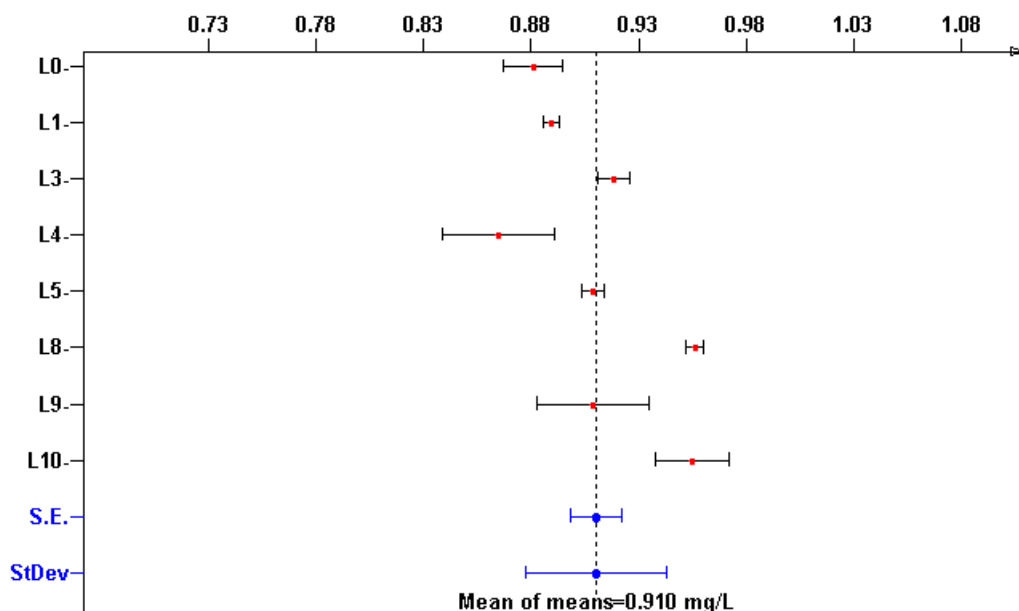
The tables in this annex contain also the datasets that were discarded for technical reasons. These data are presented in *italics* and are given for informative purposes only. They are not reported in the graphs. Small letters are added to the tags of laboratories reporting results with two different techniques.

The bars in the graphs represent *s*, standard deviation of the measurement results. The X axis range covers approximately $\pm 20\%$ of the mean.

Ammonium

lab code	Replicates [mg/L]						mean	<i>s</i>
L0	0.89	0.887	0.899	0.88	0.863	0.866	0.881	0.014
L1	0.887	0.886	0.886	0.893	0.891	0.894	0.890	0.004
L2	<i>1.09</i>	<i>1.13</i>	<i>1.08</i>	<i>1.18</i>	<i>1.08</i>	<i>1.03</i>	<i>1.098</i>	<i>0.051</i>
L3	0.91	0.92	0.93	0.92	0.92	0.91	0.918	0.008
L4	0.842	0.886	0.892	0.845	0.837	0.886	0.865	0.026
L5	0.906	0.903	0.908	0.910	0.918	0.906	0.909	0.005
L7	<i>0.96</i>	<i>0.954</i>	<i>0.955</i>	<i>0.959</i>	<i>0.96</i>	<i>0.958</i>	<i>0.958</i>	<i>0.003</i>
L8	0.963	0.953	0.958	0.953	0.953	0.958	0.956	0.004
L9	0.920	0.938	0.878	0.935	0.894	0.886	0.909	0.026
L10	0.944	0.938	0.939	0.978	0.970	0.961	0.955	0.017

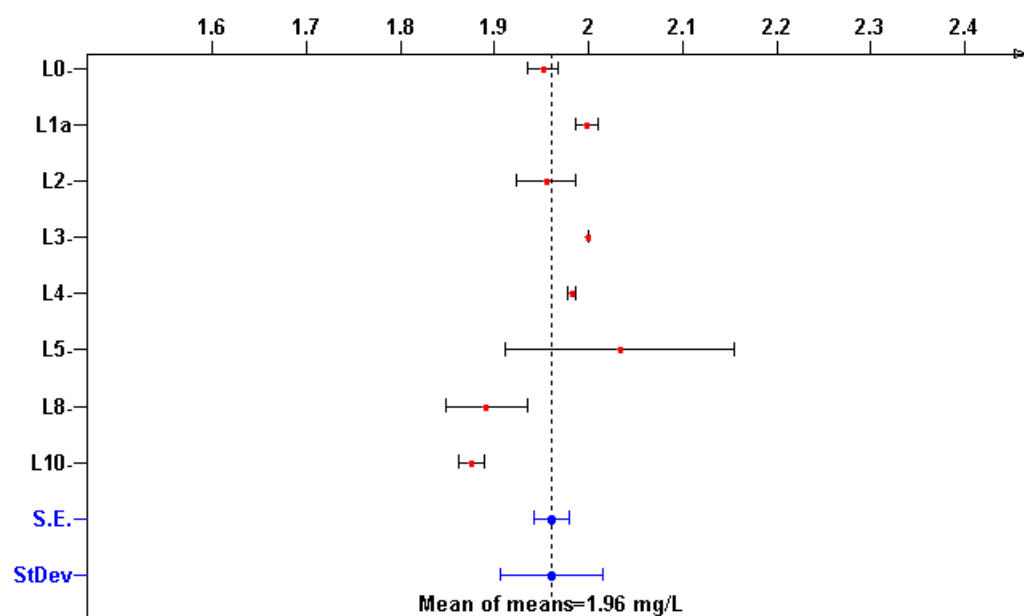
Laboratory means and their standard deviation



Chloride

lab code	Replicates [mg/L]						mean	s
L0	1.96	1.96	1.96	1.95	1.92	1.96	1.952	0.016
L1a	1.9834	2.0186	2.0064	1.9943	1.9931	1.9943	1.998	0.012
L2	1.95	1.92	1.97	1.92	1.97	2.00	1.955	0.031
L3	2.0	2.0	2.0	2.0	2.0	2.0	2.000	0.000
L4	1.985	1.988	1.984	1.980	1.976	1.984	1.983	0.004
L5	2.0	2.1	2.2	2.1	1.9	1.9	2.033	0.121
L7	1.775	1.819	1.836	1.679	1.723	1.84	1.779	0.066
L8	1.93	1.92	1.94	1.84	1.86	1.86	1.892	0.043
L9	1.94	1.92	1.93	1.89	1.9	1.89	1.912	0.021
L10	1.86	1.87	1.87	1.87	1.90	1.88	1.875	0.014
L1b	0.674	2.274	1.845	1.750	1.697	1.235	1.579	0.554

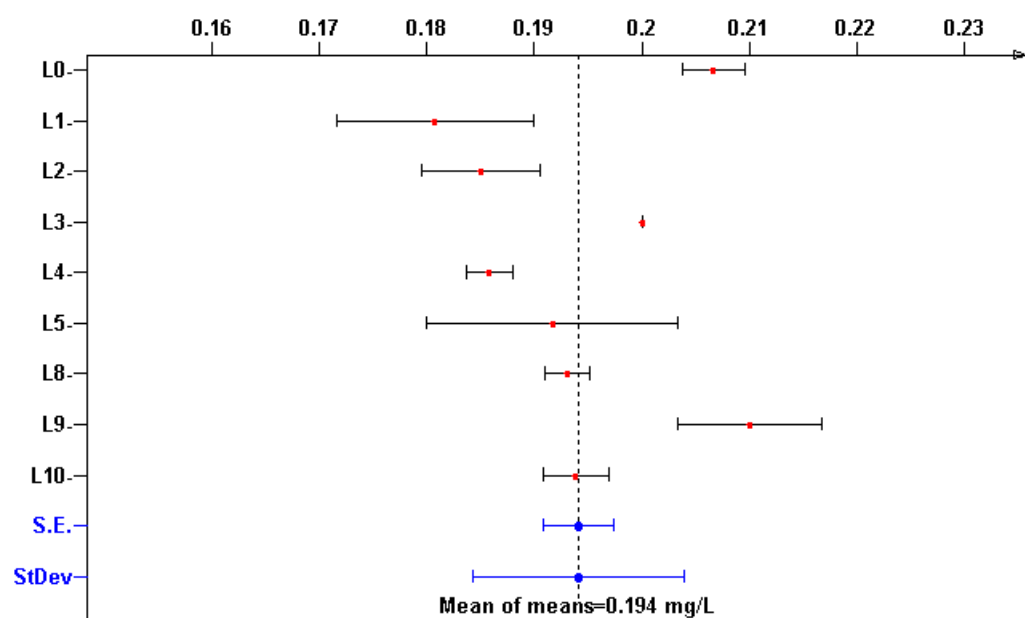
Laboratory means and their standard deviations



Fluoride

lab code	Replicates [mg/L]						mean	<i>s</i>
L0	0.209	0.21	0.208	0.202	0.205	0.206	0.207	0.003
L1	0.1914	0.1890	0.1866	0.1740	0.1732	0.1704	0.181	0.009
L2	0.18	0.19	0.18	0.19	0.18	0.19	0.185	0.005
L3	0.2	0.2	0.2	0.2	0.2	0.2	0.200	0.000
L4	0.184	0.187	0.188	0.185	0.183	0.188	0.186	0.002
L5	0.19	0.2	0.21	0.19	0.18	0.18	0.192	0.012
L7	0.16	0.15	0.15	0.16	0.16	0.17	0.158	0.008
L8	0.196	0.194	0.192	0.192	0.194	0.19	0.193	0.002
L9	0.210	0.218	0.210	0.203	0.202	0.217	0.210	0.007
L10	0.194	0.19	0.193	0.192	0.199	0.195	0.194	0.003

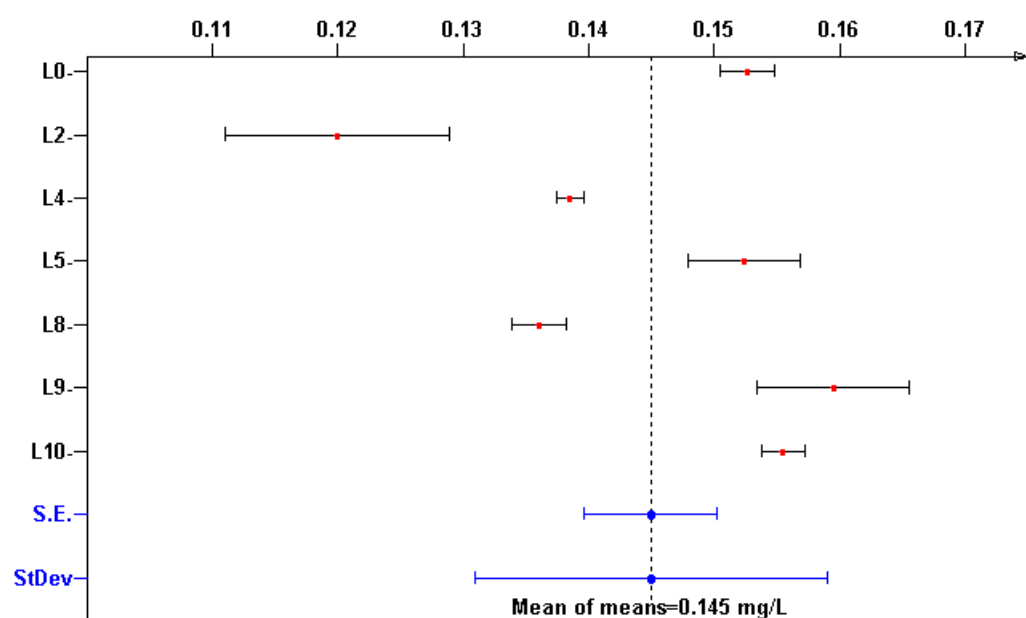
Laboratory means and their standard deviations



Magnesium

lab code	Replicates [mg/L]						mean	s
L0	0.15	0.15	0.153	0.155	0.154	0.154	0.153	0.002
L1	0.1142	0.1140	0.1108	0.1428	0.1525	0.1449	0.130	0.019
L2	0.12	0.12	0.11	0.13	0.13	0.11	0.120	0.009
L3	0.09	0.10	0.12	0.09	0.12	0.12	0.107	0.015
L4	0.140	0.139	0.139	0.138	0.138	0.137	0.139	0.001
L5	0.149	0.147	0.151	0.156	0.152	0.159	0.152	0.004
L7	0.2177	0.1542	0.2109	0.1556	0.1465	0.1553	0.173	0.032
L8	0.136	0.1375	0.1395	0.134	0.135	0.134	0.136	0.002
L9	0.1567	0.1549	0.1545	0.1649	0.1692	0.1567	0.159	0.006
L10	0.154	0.154	0.154	0.157	0.156	0.158	0.156	0.002

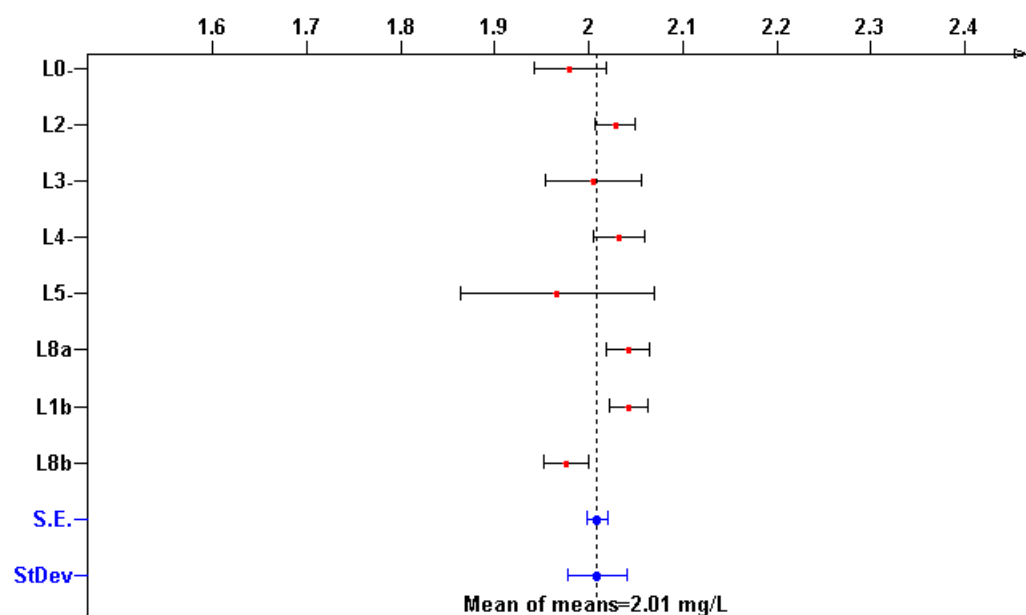
Laboratory means and their standard deviations



Nitrate

lab code	Replicates [mg/L]						mean	s
L0	2.02	2.03	1.97	1.96	1.93	1.97	1.980	0.038
L1a	1.550	1.532	1.580	1.997	2.032	2.036	1.788	0.257
L2	2.04	2.04	2.03	2.05	1.99	2.02	2.028	0.021
L3	2.10	2.00	2.00	2.00	1.95	1.98	2.005	0.050
L4	2.021	2.023	2.018	2.082	2.005	2.044	2.032	0.027
L5	2	2	2.1	2	1.8	1.9	1.967	0.103
L7	1.938	1.905	1.866	2.01	2.13	2.052	1.984	0.099
L8a	2.0203	2.0732	2.0701	2.0334	2.0245	2.0289	2.042	0.024
L9	2.014	2.019	1.908	2.001	2.045	2.058	2.008	0.053
L10	2.03	2.00	2.00	2.00	2.10	2.06	2.032	0.041
L1b	2.066	2.057	2.048	2.014	2.022	2.045	2.042	0.020
L8b	1.953	1.955	1.972	2	2	-	1.976	0.023

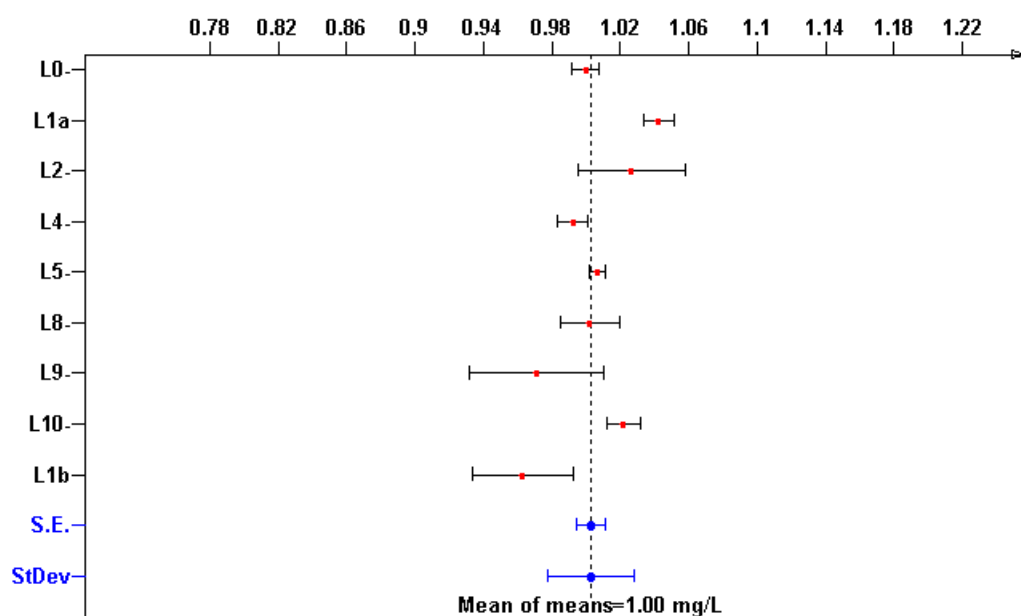
Laboratory means and their standard deviations



Ortho-phosphate

lab code	Replicates [mg/L]						mean	s
L0	0.993	0.988	1.007	1.006	1.003	1	1.000	0.008
L1a	1.054	1.045	1.045	1.048	1.03	1.033	1.043	0.009
L2	0.99	1.04	0.999	1.05	1.01	1.07	1.027	0.032
L3	1.00	0.93	1.00	1.00	1.10	0.95	0.997	0.059
L4	0.980	0.987	0.991	1.002	0.990	1.003	0.992	0.009
L5	1.008	1.003	1.010	0.999	1.010	1.011	1.007	0.005
L7	1.03	0.996	0.999	0.99	1.002	0.99	1.001	0.015
L8	1.000	1.006	1.027	1.012	0.990	0.978	1.002	0.017
L9	0.941	0.932	0.935	0.99	1.006	1.021	0.971	0.040
L10	1.03	1.01	1.03	1.02	1.03	1.01	1.022	0.010
L1b	0.989	0.983	0.992	0.945	0.92	0.948	0.963	0.029

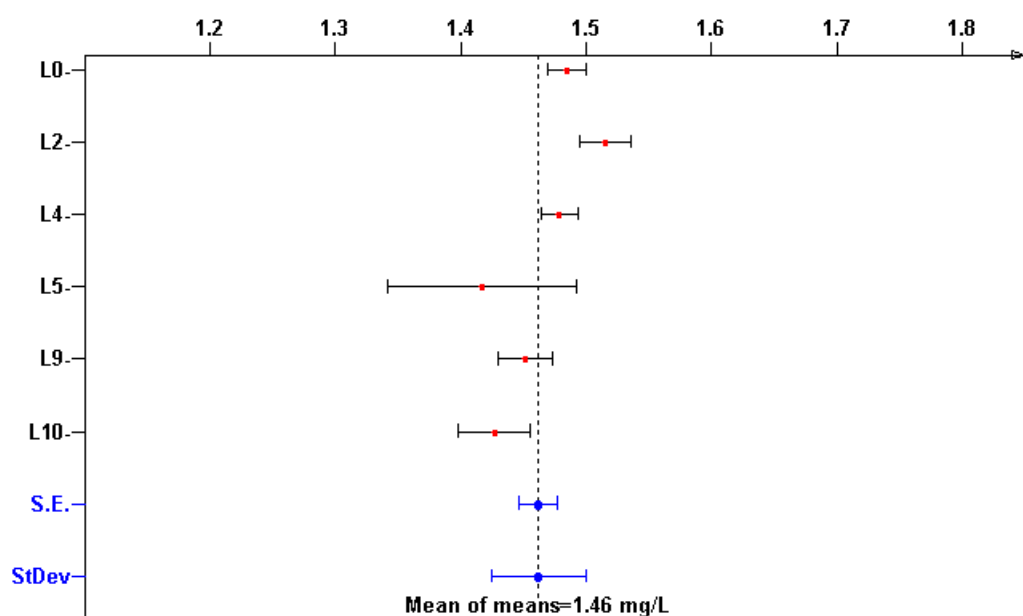
Laboratory means and their standard deviations



Sulfate

lab code	Replicates [mg/L]						mean	s
L0	1.5	1.48	1.49	1.48	1.46	1.5	1.485	0.015
L1a	0.782	0.757	0.599	0.736	0.719	0.738	0.722	0.064
L2	1.53	1.50	1.53	1.53	1.48	1.52	1.515	0.021
L3	2.00	1.96	2.00	1.98	2.00	2.00	1.990	0.021
L4	1.47	1.47	1.50	1.46	1.48	1.49	1.478	0.015
L5	1.4	1.4	1.5	1.5	1.3	1.4	1.417	0.075
L7	1.498	1.398	1.399	1.434	1.486	1.416	1.439	0.044
L8	1.82	1.82	1.82	1.658	1.677	1.636	1.739	0.090
L9	1.43	1.48	1.47	1.44	1.43	1.46	1.452	0.021
L10	1.39	1.41	1.41	1.44	1.47	1.44	1.427	0.029
L1b	1.243	1.243	1.235	1.226	1.212	1.236	1.233	0.012

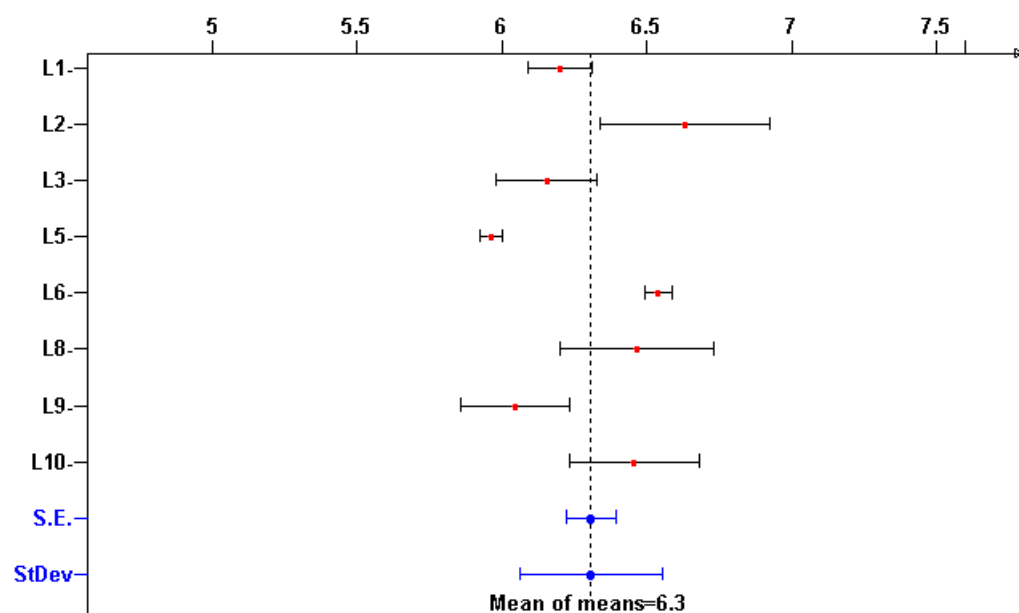
Laboratory means and their standard deviations



pH

lab code	Replicates						mean	s
L0	7.202	7.004	7.005	6.96	6.996	7.192	7.060	0.108
L1	6.16	6.02	6.33	6.16	6.26	6.28	6.20	0.11
L2	7.02	6.88	6.65	6.63	6.3	6.3	6.63	0.29
L3	6.37	6.34	6.06	6.2	5.98	5.98	6.16	0.18
L4	6.16	6.05	5.94	5.90	6.14	6.08	6.05	0.11
L5	5.95	5.94	5.94	5.92	6.02	6	5.96	0.04
L6	6.532	6.6	6.577	6.523	6.544	6.465	6.540	0.047
L7	6.19	6.19	6.05	6.05	6.49	6.4	6.23	0.18
L8	6.18	6.27	6.33	6.67	6.88	6.45	6.46	0.27
L9	5.94	5.83	5.98	5.97	6.28	6.28	6.05	0.19
L10	6.71	6.74	6.28	6.21	6.35	6.45	6.46	0.22

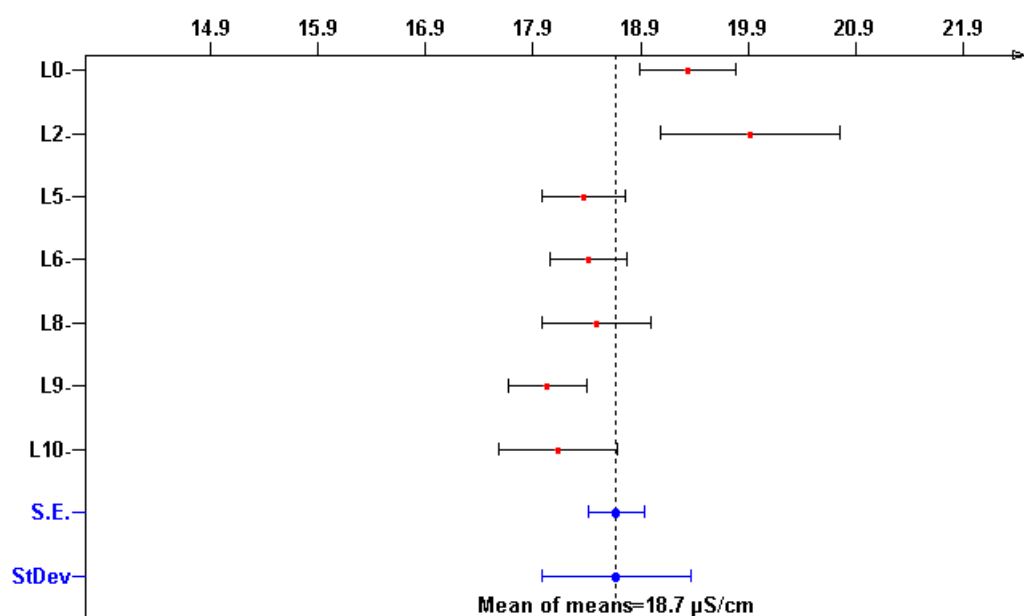
Laboratory means and their standard deviations



Conductivity

lab code	Replicates [$\mu\text{S}/\text{cm}$]						mean	<i>s</i>
L0	19.6	19.4	19.4	19.9	18.6	19.1	19.333	0.446
L1	31.0	30.9	26.0	24.8	23.7	26.0	27.067	0.446
L2	21.1	20.8	19.7	19.5	19.4	19.0	19.917	0.838
L3	18.2	24.6	40.4	18.8	39.1	40.1	30.200	10.831
L4	17.79	17.79	17.42	17.43	17.56	17.66	17.608	0.166
L5	17.98	18.28	18.08	18.38	18.42	19.08	18.370	0.388
L6	18.84	18.66	18.7	18.17	18.15	17.98	18.417	0.358
L7	18.19	18.22	18.2	18.31	21.73	21.11	19.293	1.659
L8	18.22	17.95	17.95	19.12	18.85	18.85	18.490	0.512
L9	17.8	17.8	17.8	17.8	18.5	18.5	18.033	0.361
L10	18.8	18.8	17.5	17.8	17.8	18.1	18.133	0.550

Laboratory means and their standard deviations



EUR 24426 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: Certification of the mass concentrations of ammonium, chloride, fluoride, magnesium, nitrate, *ortho*-phosphate, sulfate, and of pH and conductivity in simulated rainwater

Author(s): M. Ricci, E. de Vos, A. Oostra, H. Emteborg, A. Held

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Abstract

This report presents the preparation and certification of the simulated rainwater certified reference material ERM-CA408. All the steps required for the production of this water-matrix certified reference material are described in detail, from the preparation of the simulated rainwater until the characterization exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2]. Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison among several experienced laboratories. IRMM organised and coordinated all the phases of this project including evaluation of data. The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, see below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and stability.

SIMULATED RAINWATER		
	Mass Concentration	
	Certified value ²⁾ [mg/L]	Uncertainty ³⁾ [mg/L]
Ammonium	0.910	0.028
Chloride ¹⁾	1.96	0.07
Fluoride	0.194	0.008
Magnesium	0.145	0.022
Nitrate	2.01	0.09
<i>Ortho</i> -phosphate	1.00	0.05
Sulfate ¹⁾	1.46	0.04
	Electrochemical property	
	Certified value ²⁾ [μS/cm]	Uncertainty ³⁾ [μS/cm]
Conductivity (20 °C)	18.7	1.8
	Chemical property	
	Certified value ²⁾	Uncertainty ³⁾
pH (20 °C)	6.3	0.6
1) as obtained by ion chromatography coupled with conductimetric detection 2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values and their uncertainties are traceable to the International System of Units (SI). 3) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) with a coverage factor $k = 2$, corresponding to a level of confidence of about 95 %.		

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